

FORM PTO-1390 (REV. 11-2000)		U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE		ATTORNEY'S DOCKET NUMBER 6680-010	
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371				U.S. APPLICATION NO. (If known, see 37 CFR 1.5) 09/937090	
INTERNATIONAL APPLICATION NO. PCT/FROO/00614		INTERNATIONAL FILING DATE March 14, 2000		PRIORITY DATE CLAIMED March 24, 1999	
TITLE OF INVENTION METHOD FOR COPOLYMERIZATION AND RESULTING COPOLYMERS					
APPLICANT(S) FOR DO/EO/US <u>Guillaume Desurmont; Hajime Yasuda; Jean Malinge</u>					
Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:					
<ol style="list-style-type: none">1. <input checked="" type="checkbox"/> This is a FIRST submission of items concerning a filing under 35 U.S.C. 371.2. <input type="checkbox"/> This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371.3. <input checked="" type="checkbox"/> This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (21) indicated below.4. <input checked="" type="checkbox"/> The US has been elected by the expiration of 19 months from the priority date (Article 31).5. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371(c)(2))<ol style="list-style-type: none">a. <input checked="" type="checkbox"/> is attached hereto (required only if not communicated by the International Bureau).b. <input type="checkbox"/> has been communicated by the International Bureau.c. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US).6. <input checked="" type="checkbox"/> An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).<ol style="list-style-type: none">a. <input checked="" type="checkbox"/> is attached hereto.b. <input type="checkbox"/> has been previously submitted under 35 U.S.C. 154(d)(4).7. <input type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))<ol style="list-style-type: none">a. <input type="checkbox"/> are attached hereto (required only if not communicated by the International Bureau).b. <input type="checkbox"/> have been communicated by the International Bureau.c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired.d. <input type="checkbox"/> have not been made and will not be made.8. <input type="checkbox"/> An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).9. <input type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).10. <input checked="" type="checkbox"/> An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).					
Items 11 to 20 below concern document(s) or information included:					
<ol style="list-style-type: none">11. <input type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98.12. <input type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.13. <input checked="" type="checkbox"/> A FIRST preliminary amendment14. <input type="checkbox"/> A SECOND or SUBSEQUENT preliminary amendment.15. <input type="checkbox"/> A substitute specification.16. <input type="checkbox"/> A change of power of attorney and/or address letter.17. <input type="checkbox"/> A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.18. <input type="checkbox"/> A second copy of the published international application under 35 U.S.C. 154(d)(4).19. <input type="checkbox"/> A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).20. <input checked="" type="checkbox"/> Other items or information: -International Search Report					

U.S. APPLICATION NO. (37 CFR 1.53) 09/937090		INTERNATIONAL APPLICATION NO. PCT/FR00/00614		ATTORNEY'S DOCKET NUMBER 6680-010	
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21. <input checked="" type="checkbox"/> The following fees are submitted: BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)): Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO. \$1000.00 International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO \$860.00 International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$710.00 International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) \$690.00 International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) \$100.00 ENTER APPROPRIATE BASIC FEE AMOUNT =				CALCULATIONS PTO USE ONLY <div style="display: flex; justify-content: space-between;"> \$ 860.00 </div>	
Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(e)).				<div style="display: flex; justify-content: space-between;"> \$ </div>	
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	\$	
Total claims	29 - 20 =	9	x \$18.00	\$ 162.00	
Independent claims	4 - 3 =	1	x \$80.00	\$ 80.00	
MULTIPLE DEPENDENT CLAIM(S) (if applicable)				+ \$270.00	
TOTAL OF ABOVE CALCULATIONS =				\$ 1,102.00	
<input type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are reduced by 1/2.				+	
SUBTOTAL =				\$ 1,102.00	
Processing fee of \$130.00 for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f)).				\$	
TOTAL NATIONAL FEE =				\$ 1,102.00	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property +				\$	
TOTAL FEES ENCLOSED =				\$	
				Amount to be refunded:	\$
				charged:	\$

a. ☐ A check in the amount of \$ _____ to cover the above fees is enclosed.

b. ☒ Please charge my Deposit Account No. 50-0521 in the amount of \$ 1,102.00 to cover the above fees. A duplicate copy of this sheet is enclosed.

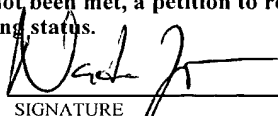
c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 50-0521. A duplicate copy of this sheet is enclosed.

d. ☐ Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. **Credit card information should not be included on this form.** Provide credit card information and authorization on PTO-2038.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137 (a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

Nada Jain, Esq.
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 200 Park Avenue
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 SIGNATURE
 Nada Jain
 NAME
 41,431
 REGISTRATION NUMBER



09937090 PCT/FR00/00614 12 FEB 2002

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CERTIFICATE OF MAILING

I hereby certify that this correspondence is being deposited with the United States Post Office as first class mail in an envelope addressed to: Commissioner for Patents, Washington, D.C. 20231, on

Date

Name:

Signature:

1-31-02
Melissa Scanzillo
Melissa Scanzillo
Clifford Chance Rogers & Wells LLP

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Docket No. 6680-010

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of: Desurmont et al.

Int'l Filing Date: March 14, 2000

Group Art Unit: to be determined

Serial No: 09/937,090

Examiner: to be determined

For: METHOD FOR COPOLYMERIZATION AND RESULTING COPOLYMERS

Commissioner for Patents
Washington, D.C. 20231

SUPPLEMENTAL PRELIMINARY AMENDMENT
FOR INDICATING PRIORITY CLAIM UNDER 37 CFR 1.78

Sir:

Prior to the first Office Action, kindly amend the application as follows.

IN THE SPECIFICATION:

Please amend the specification as follows:

Page 1, before the first line, insert:

--This application claims priority to PCT/FR00/00614 filed March 14, 2000, which claims priority to French Patent Application No. 9903669 filed March 24, 1999.--

REMARKS

Entry of the above amendment is respectfully requested. Because the above-referenced application entered the national stage from an international application filed under 35 U.S.C. 363 before

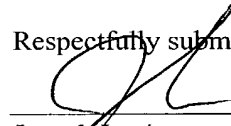
November 29, 2000, the submission of a reference to a priority claim is timely and no fee is required.

Date:

1/30/02

Clifford Chance Rogers & Wells LLP
200 Park Avenue
New York, NY 10166-0153
Telephone: (212) 878-8564

Respectfully submitted,



Joseph Levi
Reg. No. 41,152

Docket No. 6680-010

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants: Desurmont et al.
Int'l App. No.: PCT/FR00/00614 Int'l Filing Date: March 14, 2000
U.S. Serial No.: To Be Assigned Filing Date: Herewith
For: METHOD FOR COPOLYMERIZATION AND RESULTING COPOLYMERS

Assistant Commissioner for Patents
Box PCT
Washington, DC 20231

PRELIMINARY AMENDMENT

Sir:

Prior to the examination of the above-identified application, please amend the application as follows.

In the claims:

Please cancel claims 1-25.

Please add new claims 26-55 as shown on the attached.

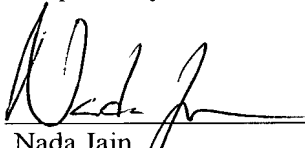
REMARKS

Claims 1-25 have been cancelled and new claims 26-55 have been added to conform the claim language to the U.S. patent practice. No new matter has been added.

Early and favorable consideration of this application is respectfully requested.

Respectfully submitted,

Dated: Sept. 21, 2001


Nada Jain
Reg. No. 47,431

MAILING ADDRESS:

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NEW CLAIMS

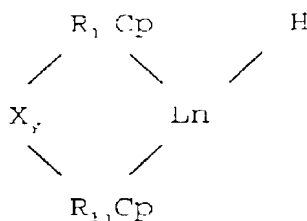
Applicants : Desurmont et al.

Int'l App. No. : PCT/FR00/00614

Int'l Filing Date : March 14, 2000

Our Ref. : 6680-010

26. A method of preparing block copolymers, comprising the steps of polymerizing a first monomer consisting of an alpha-olefin containing from 3 to 20 carbon atoms into a first, isotactic block, using a catalyst, then polymerizing at least one second monomer, said catalyst being in the form of a hydride complex of a trivalent metal from the rare earth group, having the formula I:



in which:

Cp is a cyclopentadienyl radical;

R_1 , identical or different at each occurrence, is a substituent of the cyclopentadienyl group and is an alkyl radical or a silicon-containing hydrocarbon radical, unsubstituted and containing from 1 to 6 carbon atoms;

j , identical or different at each occurrence, is 1, 2 or 3;

X is a divalent alkylene radical containing from 1 to 20 carbon atoms or $\text{Si}(\text{R})_2$ in +which

R is an alkyl radical having from 1 to 4 carbon atoms;

y is 1 or 2;

Ln is Y or Sm.

27. The method as claimed in claim 26, wherein, in the formula I, $R_1\text{Cp}$ is the group 2-Me₃Si,4-Me₂tBuSiCp or the group 2-Me₃Si,4-tBuCp.

28. The method as claimed in claim 26, wherein the catalyst is Me₂Si(2-Me₃Si,4-Me₂tBuSiCp)₂YH or Me₂Si(2-Me₃Si,4-tBuCp)₂SmH.

29. The method as claimed in claim 26, wherein the catalyst is racemic.

30. The method as claimed in claim 26, wherein the catalyst is generated in situ in the presence of at least one portion of the first monomer.

NEW CLAIMS

Applicants : Desurmont et al.

Int'l App. No. : PCT/FR00/00614

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Our Ref. : 6680-010

31. The method as claimed in claim 26, wherein the catalyst is prepared by hydrogenation of the alkyl precursor.
32. The method as claimed in claim 26, wherein the blocks are homopolymers or random copolymers.
33. The method as claimed in claim 26, wherein the block copolymer comprises a block of the second monomer which is a vinyl, vinylidene or lactone compound.
34. The method as claimed in claim 33, wherein the vinyl or vinylidene compound is represented by the formula $H_2C=CR'Z$ in which R' is hydrogen or an alkyl radical having from 1 to 12 carbon atoms and Z is an electron-withdrawing radical.
35. The method as claimed in claim 34, wherein the vinyl or vinylidene compound is an ester of an unsaturated carboxylic acid.
36. The method as claimed in claim 33, wherein the poly-alpha-olefin is crystalline.
37. The method as claimed in claim 26, wherein the second monomer is polar.
38. The method as claimed in claim 26, for preparing a poly-alpha-olefin/PMMA or poly-alpha-olefin/polylactone copolymer.
39. The method as claimed in claim 26, wherein the block copolymer comprises a block of the second monomer which is an alpha-olefin.
40. The method as claimed in claim 39, wherein the first poly-alpha-olefin is crystalline and the second poly-alpha-olefin is crystalline.
41. The method as claimed in claim 40, for preparing a PP/PE copolymer.

NEW CLAIMS

Applicants : Desurmont et al.

Int'l App. No. : PCT/FR00/00614

Int'l Filing Date : March 14, 2000

Our Ref. : 6680-010

42. The method as claimed in claim 38, wherein the first poly-alpha-olefin is crystalline and the second poly-alpha-olefin is amorphous.
43. The method as claimed in claim 42, for preparing a PP/EP copolymer.
44. The method as claimed in claim 26, wherein the block copolymer comprises a first iPP block.
45. The method as claimed in claim 26, wherein the catalyst is racemic and is generated in situ in the presence of at least one portion of the first monomer.
46. The method as claimed in claim 45, wherein the catalyst is prepared by hydrogenation of the alkyl precursor.
47. A copolymer comprising a first block of a crystalline polyolefin derived from an alpha-olefin containing from 3 to 20 carbon atoms and a second block of an amorphous polyolefin, with the exception of a PP/EP copolymer having a molecular mass M_n of less than or equal to 16 000 and a polydispersity index of between 3 and 3.3.
48. The copolymer as claimed in claim 47, which is a PP/EP copolymer.
49. The copolymer as claimed in claim 47, wherein the first block is isotactic.
50. The copolymer as claimed in claim 47, wherein the blocks are homopolymers or random copolymers.
51. A copolymer comprising a first block of a crystalline polyolefin derived from an alpha-olefin containing from 3 to 20 carbon atoms and a second block of a crystalline polyolefin.
52. The copolymer as claimed in claim 51, wherein the first block is isotactic.
53. The copolymer as claimed in claim 51, wherein the blocks are homopolymers or random copolymers.

NEW CLAIMS

Applicants : Desurmont et al.

Int'l App. No. : PCT/FR00/00614

Int'l Filing Date : March 14, 2000

Our Ref. : 6680-010

54. A copolymer comprising a first block of an amorphous polyolefin derived from an alpha-olefin containing from 3 to 20 carbon atoms and a second block of an amorphous polyolefin.

55. The copolymer as claimed in claim 54, wherein the blocks are homopolymers or random copolymers.

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METHOD FOR COPOLYMERIZATION AND
RESULTING COPOLYMERS

The present invention relates to a novel method
5 of preparing block copolymers, and to certain of these
block copolymers.

Block copolymers are widely known. However, it
is also known that it is difficult to prepare block
copolymers one of whose blocks is a polyolefin (PO),
10 especially if the desire is that the alpha-olefin
should be inserted in a regular manner in order to give
a stereoregular and/or regioregular copolymer. It is
also known that it is (virtually) impossible to prepare
block copolymers whose two blocks are polyolefins,
15 whether crystalline or amorphous.

Yamahiro et al., Macromol. Chem. Phys. 200,
134-141 (1999), describes a process of stopped-flow
polymerization for obtaining "true" PP/EP block
copolymers. However, the copolymers produced are
20 limited in terms of molecular mass, since they have a
molecular weight Mn of less than or equal to 16 000 and
a polydispersity index of between 3.0 and 3.3. Other
molecular mass characteristics are excluded by this
type of technique: in particular, higher molecular
25 masses cannot be attained, since they are a function of
the polymerization time, which can only be short (of
the order of from 0.1 to 0.2 s) and in any case less
than the growth time of a chain; in particular, also,
lower polydispersity indexes cannot be attained, since
30 stopped-flow polymerization is not a true poly-
merization with living species, but comprises a large
number of transfer reactions.

Therefore, there is to date no true PP/EP
copolymer, with a PP block and an EP block linked
35 together, which has a sufficient molecular mass. This
PP/EP copolymer is a crystalline PO/amorphous PO
copolymer, which would find advantageous application in

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PP/EP polymer blends. In these blends, the crystalline PP forms the continuous phase, which is modified by the addition of EP copolymer (more specifically EPR, which is elastomeric) which forms a nodular disperse phase. A
5 true copolymer added to this blend would play a part similar to that played by an emulsifier in emulsions, improving the compatibility of the phases, and ultimately would enhance the impact/rigidity trade-off.

This same problem of difficulty in preparing
10 "true" block copolymers occurs with copolymers one of whose blocks is a block of a polar monomer, such as MMA.

The patent application EP-A-0634429 in the name of Mitsui describes the preparation of block copoly-
15 mers, one block being a polyolefin and one block being derived from a vinyl, vinylidene or lactone monomer. The catalyst used is an alkyl complex of a metal from the rare earth group, with bridged cyclopentadiene rings (bridged by a dimethylsilylene group). This
20 document describes in particular the catalyst $\text{Me}_2\text{Si}(2\text{-Me}_3\text{Si}, 4\text{-tBuCp})_2\text{YCH}(\text{SiMe}_3)_2$, with - optionally - a THF-type donor complexed to the metal. The copolymers obtained, however, are not satisfactory, since the polyolefin fraction represents too low a fraction of
25 the final copolymer. Moreover, if the polydispersity values appear to be acceptable, it is only because these values are derived from the PMMA fraction, representing the quasitotality of the copolymer. Moreover, the catalysts do not in fact provide true
30 copolymers. In effect, extensive transfer reactions (that is, the reactions which put an end to the living nature of the polymerization) lead to the formation not of true copolymers but of a mixture of homopolymers and copolymers. Moreover, the reaction times are fairly
35 long.

The article by Yasuda et al., Tetrahedron, Vol. 51, No. 15, pp. 4563-4570, 1995, describes hydride derivatives of lanthanides in the form of a complex

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with bridged cyclopentadiene rings (bridged by a dimethylsilylene group), these cyclopentadiene rings carrying substituents which have a significant steric bulk ("bulky substituent"). This document describes in particular the hydride catalyst $\text{Me}_2\text{Si}(2\text{-Me}_3\text{Si}, 4\text{-Me}_2\text{tBuSiCp})_3\text{YH}$ (represented in its dimer form). These compounds are obtained in situ by hydrogenolysis of the starting alkyl derivative, and are then used for the polymerization of alpha-olefins. Although such compounds are described as having an alpha-olefin polymerization activity greater than that of the alkyl derivatives from which they are derived, the polymerization times are still very long, of the order of half a day or a day.

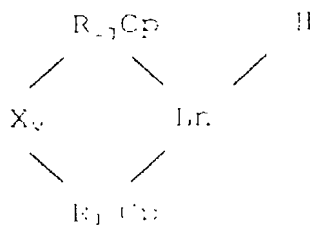
These hydride catalysts also have the classic disadvantage of hydrides, namely that hydride derivatives are known to be unstable and to break down rapidly at high temperature.

The search is therefore on for an effective method of preparing block copolymers: particularly, on the one hand, copolymers one of whose blocks includes a polar fraction, and, on the other hand, copolymers whose two blocks are polyolefins.

The invention accordingly provides a method of preparing block copolymers, comprising the steps of polymerizing a first monomer using an organolanthanide catalyst in which said catalyst is in the form of a hydride complex of a trivalent metal from the rare earth group, then polymerizing at least one second monomer.

In one embodiment, the hydride complex of a trivalent metal from the rare earth group has the formula I:

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in which:

- Cp is a cyclopentadienyl radical;
 R₁, identical or different at each occurrence,
 5 is a substituent of the cyclopentadienyl group
 and is an alkyl radical or a silicon-containing
 hydrocarbon radical, containing from 1 to
 20 carbon atoms, and with the Cp ring to which
 it is linked optionally forming an indenyl or
 fluorenyl ring system, it being possible
 10 optionally for each R₁ to be substituted;
 j, identical or different at each occurrence,
 is an integer from 1 to 5 inclusive;
 X is a divalent alkylene radical or a divalent,
 15 silicon-containing hydrocarbon radical, con-
 taining from 1 to 20 carbon atoms, optionally
 containing other heteroatoms such as oxygen;
 y is 1 or 2;
 Ln is a trivalent metal from the rare earth
 20 group, selected from Y, Sc, La, Ce, Pr, Nd, Pm, Sm, Eu,
 Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu.

In one embodiment, in the formula I, X is
 Si(R)₂ in which R is an alkyl radical having from 1 to
 4 carbon atoms.

- 25 In one embodiment, in the formula I, R₁ is an
 alkyl radical or a silicon-containing hydrocarbon
 radical, containing from 1 to 6 carbon atoms, which is
 unsubstituted, and j is 1, 2 or 3.

- In one embodiment, in the formula I, R_{1j}Cp is
 30 the group 2-Me₃Si,4-Me₂tBuSiCp or the group
 2-Me₃Si,4-tBuCp.

In one embodiment, in the formula I, Ln is Y or

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Sm.

In one embodiment, the catalyst is $\text{Me}_2\text{Si}(2\text{-Me}_3\text{Si}, 4\text{-Me}_2\text{tBuSiCp})_2\text{YH}$ or $\text{Me}_2\text{Si}(2\text{-Me}_3\text{Si}, 4\text{-tBuCp})_2\text{SmH}$.

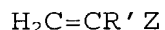
5 In one embodiment, the catalyst is racemic.

In one embodiment, the catalyst is generated in situ in the presence of at least one portion of the first monomer.

10 In one embodiment, the blocks are homopolymers or random copolymers.

In one embodiment, the block copolymer comprises a block of the first monomer which is an alpha-olefin and a block of the second monomer which is a vinyl, vinylidene or lactone compound.

15 In this embodiment, the vinyl or vinylidene compound is represented by the formula



20 in which R' is hydrogen or an alkyl radical having from 1 to 12 carbon atoms and Z is an electron-withdrawing radical.

In this embodiment, the vinyl or vinylidene compound is an ester of an unsaturated carboxylic acid.

In this embodiment, the polyolefin is crystalline.

25 In one embodiment, the second monomer is polar.

In one embodiment, the method is for preparing a PO/PMMA or PO/PL copolymer.

In this embodiment, the PO block is an iPO block.

30 In one embodiment, the block copolymer comprises a block of the first monomer which is a first alpha-olefin and a block of the second monomer which is a second alpha-olefin.

35 In a variant of this embodiment, the first polyolefin is crystalline and the second polyolefin is crystalline.

In this variant, the copolymer is a PP/PE copolymer.

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In another variant of this embodiment, the first polyolefin is crystalline and the second polyolefin is amorphous.

In this variant, the copolymer is a PP/EP
5 copolymer.

In one embodiment, the PP block is an iPP block.

The invention also provides a copolymer comprising a first block of a crystalline polyolefin
10 and a second block of an amorphous polyolefin, with the exception of a PP/EP copolymer having a molecular mass M_n of less than or equal to 16 000 and a polydispersity index of between 3 and 3.3.

In one embodiment, the copolymer is a PP/EP
15 copolymer, particularly one in which the PP block is an iPP block.

The invention also provides a copolymer comprising a first block of a crystalline polyolefin and a second block of a crystalline polyolefin.

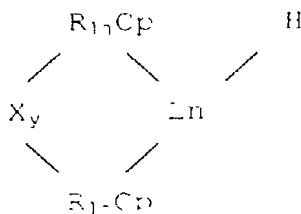
20 The invention also provides a copolymer comprising a first block of an amorphous polyolefin and a second block of an amorphous polyolefin.

In one embodiment, the blocks are homopolymers or random copolymers.

25 The invention is now described in greater detail in the following description.

Catalyst.

The catalyst is an organolanthanide in the form of a hydride complex of a trivalent metal from the rare
30 earth group (bridged); advantageously it has the formula I:



in which:

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Cp is a cyclopentadienyl radical, substituted preferably in positions 2 and 4;
R₁, identical or different at each occurrence, is a substituent of the cyclopentadienyl group
5 and is an alkyl radical or a silicon-containing hydrocarbon radical, containing from 1 to 20 carbon atoms, in particular from 1 to 6 carbon atoms, optionally forming an indenyl or fluorenyl ring system with the Cp ring to
10 which is linked, it being possible optionally for each R₁ to be substituted, for example, by up to 3 halogens;
j, identical or different at each occurrence, is an integer from 1 to 5 inclusive, in
15 particular j is 1, 2 or 3;
in particular R_{1j}Cp is the group 2-Me₃Si,4-Me₂tBuSiCp, or the group 2-Me₃Si,4-tBuCp;
X is a divalent alkylene radical or a divalent,
20 silicon-containing hydrocarbon radical, containing from 1 to 20 carbon atoms, optionally containing other heteroatoms such as oxygen, in particular of formula Si(R)₂ where R is an alkyl radical having 1 to 4 carbon atoms, in
25 particular SiMe₂;
y is 1 or 2, preferably 1;
Ln is a trivalent metal from the rare earth group, selected from Y, Sc, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu, in
30 particular Y and Sm.
Examples of catalysts are
Me₂Si(2-Me₃Si,4-Me₂tBuSiCp)₂YH and
Me₂Si(2-Me₃Si,4-tBuCp)₂SmH.

The catalyst may in fact have ligands which are
35 similar to those found for the catalysts known as "group IV" or metallocene or Kaminsky catalysts. A restricted geometry may also be envisaged, and also ligands other than those described above in relation

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with the formula I.

In one variant, the catalyst is in a racemic form. This form makes it possible to obtain isotactic polymers.

5 The catalysts of the invention in hydride form are prepared, for example, by hydrogenation from the alkyl precursor, for example by application of molecular hydrogen. The alkyl precursors are described, for example, in the document EP-A-0634429 in the name
10 of Mitsui. This operation may be performed by dissolving the alkyl starting product in a solvent (aliphatic or aromatic hydrocarbon) or suspending it in a nonsolvating hydrocarbon (aliphatic or aromatic hydrocarbon), followed by contact with molecular
15 hydrogen.

Polymerization method

 The polymerization is very effective in particular with the catalyst formed in situ in the presence of the monomer. The proof of this efficacy is
20 the exothermicity of the reaction mixture when the hydrogen is introduced, thereby demonstrating that the polymerization reaction is initiated immediately. Accordingly, each alkyl precursor leads to a potentially polymerizing hydride species, which leads
25 effectively to a polymerization. In the case of the preparation of copolymers, this formation in situ in the presence of the monomer is not necessary; it is, however, preferred.

 The method may be implemented with or without
30 solvent. In the case without solvent, it is the liquid monomer itself which plays this part. In the case with solvent, the monomer (in solution or in suspension) may be in gaseous, liquid or solid form.

 The polymerization medium may therefore be a
35 solvent, mass or gaseous medium.

 The solvent, when used, may be an aliphatic or aromatic hydrocarbon, such as toluene.

 The reaction temperature is generally between

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-78°C and 150°C, preferably from 0 to 100°C.

The reaction pressure is generally between standard pressure and 200 bar, preferably between 1 and 20 bar.

5 The reaction time is generally between a few seconds and a few hours.

The monomer (or monomer mixture) may be added in one go or gradually, in a controlled way.

10 The above conditions apply to the polymerization steps in the case both of homopolymers and copolymers, and even of terpolymers (or more if necessary).

15 In the case where copolymers are prepared, the second monomer is added, for example, directly to the reaction mixture from the first step. If a solvent has been used during this step, it may either be retained or removed by customary techniques, taking care not to degrade the living species carrying the polyolefinic chain from the first step, and optionally replaced by
20 another solvent.

The present polymerization method is efficient in that:

- 25 - it makes it possible to generate poly-alpha-olefins of controlled mass, by limiting the transfer reactions
- the poly-alpha-olefin species is living and in a second step is able to polymerize another monomer (olefinic, vinylic, etc.), in order to lead to the corresponding block
30 copolymer.

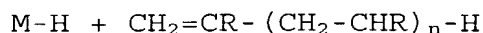
The reaction scheme is as follows (where M-H signifies the organolanthanide catalyst in hydride form).

Reaction 1 (generation of a (living) polyolefin)

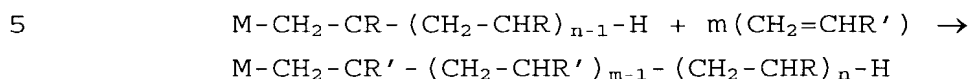
35 $M-H + n(CH_2=CHR) \rightarrow M-CH_2-CR-(CH_2-CHR)_{n-1}-H$

There is therefore maximum avoidance of the transfer reaction which produces the following final polymer species:

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Reaction 2 (addition to the living, growing polyolefin of the second monomer, to give the block copolymer, with limitation of the transfer reaction)



Advantageously, the temperature of the reaction mixture will be controlled. In order to do this, it will be possible to supply the reactor continuously with the monomer; this will make it possible in particular to limit the initial exothermicity.

In the case where it is desired to obtain copolymers, the first step will be implemented under conditions similar to those for the homopolymers, and then the second monomer will be added to the reaction mixture still containing a living species.

The (co)polymers thus obtained are separated by conventional techniques.

Polymers prepared in the invention.

The polymers prepared as claimed in the invention may be homopolymers or random copolymers (the two or more monomers being present simultaneously in the reaction mixture) or may be blocked copolymers, or even terpolymers or more if necessary.

The homopolymer, or one copolymer block, may be isotactic, particularly when the catalyst is in a racemic form (and when the monomer is prochiral).

Examples of homopolymers are poly-alpha-olefins, the olefin containing for example from 3 to 20 carbon atoms. Examples of olefins are propylene, 1-butene, 1-hexene, 1-heptene, 1-octene, 1-decene, etc.

Examples of random copolymers are the copolymers of the above olefins, or copolymers based on ethylene.

Examples of block copolymers are copolymers containing a block of the first monomer, which is an alpha-olefin, and a block of the second monomer, which is a vinyl, vinylidene or lactone compound.

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Examples of vinyl or vinylidene compounds are represented by the formula $H_2C=CR'Z$, in which R' is hydrogen or an alkyl radical having from 1 to 12 carbon atoms and Z is an electron-withdrawing radical.

5 Examples of such groups are the esters of an unsaturated carboxylic acid, especially (meth)acrylic acid. Mention may be made of methyl acrylate, ethyl acrylate, propyl acrylate, n-butyl acrylate, phenyl acrylate, methyl methacrylate, ethyl methacrylate,
10 propyl methacrylate, n-butyl methacrylate and phenyl methacrylate.

 Examples of lactones include the cyclic esters possessing from 3 to 10 carbon atoms, and are preferably propyllactone, valerolactone and capro-
15 lactone.

The polyolefin (PO) block may be crystalline, whereas the block of the second monomer may be polar.

 Specific examples of such copolymers are the copolymer PO/PMMA, especially iPO/PMMA, and PO/PL
20 (polylactone) copolymer, especially iPO/PL.

 Examples of block copolymers are copolymers containing a block of the first monomer, which is a first alpha-olefin, and a block of the second monomer, which is a second alpha-olefin.

25 Such examples of copolymers include in particular those in which the first polyolefin is crystalline and the second polyolefin is crystalline, especially a PP/PE copolymer.

 Such examples of copolymers include in
30 particular those in which the first polyolefin is crystalline and the second polyolefin is amorphous, especially a PP/EP copolymer.

 The above PP block is, for example, an iPP block.

35 The invention also provides copolymers which are "true" block copolymers, in contradistinction to the copolymers of the prior art, which provides copolymers which are mixtures.

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The molecular weight of the homopolymers or copolymers may vary within a wide range, between 500 and 10^8 , preferably between 5 000 and 10^6 . The ratio, in one copolymer, between the monomers A and B may also
5 vary within a very wide range, from 99/1 to 1/99.

The invention therefore also provides copolymers as described above.

In particular, the invention provides block copolymers of the PP/EP (crystalline PO/amorphous PO)
10 type, with the exception of those described in the publication Yamahiro et al., Macromol. Chem. Phys. 200, 134-141 (1999), namely in particular those whose molecular weight M_n is less than or equal to 16 000 and whose polydispersity index is between 3.0 and 3.3. The
15 invention therefore provides in particular block copolymers of the PP/EP type with a molecular weight greater than 16 000, in particular greater than 20 000, especially greater than 50 000, and copolymers of the PP/EP type whose polydispersity index is less than 3,
20 in particular less than 2.5, especially less than 2.

The examples which follow illustrate the invention without limiting it.

Preparation of complex 1: $\text{Me}_2\text{Si}(2\text{-Me}_3\text{Si},4\text{-tBu C}_5\text{H}_2)_2\text{Sm}(\text{THF})_2$

25 A solution of $\text{Me}_2\text{Si}(2\text{-Me}_3\text{Si},4\text{-tBu C}_5\text{H}_3)_2$ (3.01 g, 6.77 mmol) in 60 ml of THF is admixed with 8.2 ml of a 1.66M solution of nBuLi in hexane, i.e., 13.5 mmol, at 0°C. Following reaction of the mixture at ambient temperature for 6 h with stirring, 20 ml of a
30 0.68M solution of tBuOK in THF, 13.6 mmol, are added. The mixture is refluxed for 12 h and the solution is evaporated to dryness. The product is washed with twice 30 ml of hexane, leading to the potassium disalt of $\text{Me}_2\text{Si}(2\text{-Me}_3\text{Si},4\text{-tBu C}_5\text{H}_3)_2$ in the form of white powder
35 (yield = 70%). A suspension of 5.64 g (10.8 mmol) of the potassium disalt of $\text{Me}_2\text{Si}(2\text{-Me}_3\text{Si},4\text{-tBu C}_5\text{H}_3)_2$ in 80 ml of THF and 10 mmol of SmI_2 in 80 ml of THF are added at the same time to 40 ml of THF at -80°C. The

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reaction mixture is then refluxed for 12 h and the solution is subsequently evaporated to dryness. 50 ml of toluene are added to the residue and the solid obtained is separated by centrifuging. Following
 5 removal of the solvent under vacuum, the residue is extracted with twice 15 ml of THF. Recrystallization from a THF/hexane mixture leads to 1 in the form of a violet solid (yield = 35%).

Preparation of complex B: $\text{Me}_2\text{Si}(2\text{-Me}_3\text{Si},$
 10 $4\text{-Me}_2, \text{tBuSiC}_5\text{H}_2)_2\text{YCH}(\text{SiMe}_3)_2$

A solution of $\text{Me}_2\text{Si}(2\text{-Me}_3\text{Si}, 4\text{-Me}_2, \text{tBuSiC}_5\text{H}_2)_2\text{YCl}_2\text{Li}(\text{THF})_2$ (2 g, 2.3 mmol) in 60 ml of toluene is admixed with 4.5 ml of a 0.79M solution of $(\text{Me}_3\text{Si})_2\text{CHLi}$ in Et_2O , i.e., 3.5 mmol, at 0°C . The
 15 mixture is stirred from 0°C to ambient temperature for 13 hours, after which the solvent is evaporated under vacuum. 80 ml of hexane are added to the residue and the suspension is stirred for 24 hours. The insoluble solid is recovered by centrifuging and is
 20 recrystallized from hexane to give B - yield = 36%.

Preparation of complex C: $\text{Me}_2\text{Si}(2\text{-Me}_3\text{Si}, 4\text{-tBuSiC}_5\text{H}_2)_2\text{SmCH}(\text{SiMe}_3)_2$

A solution of $\text{Me}_2\text{Si}(2\text{-Me}_3\text{Si}, 4\text{-tBuC}_5\text{H}_2)_2\text{SmCl}_2\text{Li}(\text{THF})_2$ (2.3 mmol) in 60 ml of toluene is
 25 admixed with 4.5 ml of a 0.79M solution of $(\text{Me}_3\text{Si})_2\text{CHLi}$ in Et_2O , i.e., 3.5 mmol, at 0°C . The mixture is stirred from 0°C to ambient temperature for 13 hours, after which the solvent is evaporated under vacuum. 80 ml of hexane are added to the residue and the suspension is
 30 stirred for 24 hours. The insoluble solid is recovered by centrifuging and is recrystallized from hexane to give C - yield = 28%.

Example 1:

20 ml of distilled toluene are introduced,
 35 using a syringe, into a Schlenk tube (dried at 100°C for 2 h beforehand), connected to an argon line and equipped with a septum for introducing the reactants and with a magnetic stirrer. The toluene is degassed

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and then saturated with argon. Catalyst 1 (7.4 mg -
0.01 mmol) is introduced and stirring is maintained
until it has completely dissolved. Then 2 ml of
1-pentene are introduced through the septum using a
5 syringe. Polymerization is continued for 12 hours at
ambient temperature with stirring. To neutralize the
catalyst at the end of the reaction, 10 ml of methanol
are injected. The precipitated polymer is then isolated
by centrifuging, washed with twice 10 ml of methanol
10 and dried under vacuum for 3 hours. The catalytic
activity is 161 g of polymer/mol of catalyst/h. The
polymer possesses the following characteristics:
Mn = 10 600. The chain incorporation of the monomer is
isotactic (mm > 95%).

15 Example 2:

The procedure of example 1 is repeated except
that the 1-pentene is replaced by 2 ml of 1-hexene. The
catalytic activity is 138 g of polymer/mol of
catalyst/h, and the polymer possesses the following
20 characteristics: Mn = 24 600. The chain incorporation
of the monomer is isotactic (mm > 95%).

Example 3:

20 ml of distilled toluene are introduced,
using a syringe, into a Schlenk tube (dried at 100°C
25 for 2 h beforehand), connected to an argon line and
equipped with a septum for introducing the reactants
and with a magnetic stirrer. The toluene is degassed
and then saturated with argon. Catalyst B (8 mg -
0.01 mmol) is introduced and stirring is maintained
30 until it has completely dissolved. Then 2 ml of
1-pentene are introduced through the septum using a
syringe. Polymerization is continued for 12 hours at
ambient temperature with stirring. To neutralize the
catalyst at the end of the reaction, 10 ml of methanol
35 are injected. There is no precipitation of polymer.
Following evaporation of the solvent, traces of
unisolatable, low-mass oligomers are collected. The
catalytic activity is very low and is estimated to be

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less than 10 g of polymer/mol of catalyst/h.

Example 4:

20 ml of distilled toluene are introduced, using a syringe, into a Schlenk tube (dried at 100°C for 2 h beforehand), connected to an argon line and equipped with a septum for introducing the reactants and with a magnetic stirrer. The toluene is degassed and then saturated with argon. Precursor B (4 mg) is introduced and the solution is stirred at ambient temperature until its dissolution is complete. The catalytic solution is degassed three times, then a pressure of 1 bar of hydrogen is introduced. Hydrogenation is carried out at ambient temperature for 30 minutes. The solution turns from colorless to a vivid yellow. The hydrogen is subsequently driven off by a stream of argon (5 min). The reaction mixture is cooled to 0°C. Then 2 g of 1-pentene are introduced through the septum using a syringe. Polymerization is continued at 0°C for 18 hours. To neutralize the catalyst at the end of the reaction, 10 ml of methanol are injected. The precipitated polymer is then isolated by centrifuging, washed with 10 ml of methanol and dried under vacuum for 3 hours. 1.54 g of polymer are collected, corresponding to a conversion of 77% and an activity of 21 g of polymer/g of catalyst/h, said polymer possessing the following characteristics: Mn = 28 600. The chain incorporation of the monomer is isotactic (mm > 95%).

Example 5:

The procedure of example 4 is repeated, replacing the 1-pentene by 2 g of 1-hexene. The polymerization is continued at 0°C for 12 hours. 1.88 g of polymer are collected, corresponding to a conversion of 94% and an activity of 39.2 g of polymer/mol of catalyst/h, said polymer possessing the following characteristics: Mn = 53 000. The chain incorporation of the monomer is isotactic (mm > 95%).

Example 6:

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The procedure of example 5 is repeated, conducting the polymerization at 20°C rather than at 0°C. 1.98 g of polymer are collected, corresponding to a conversion of 99% and an activity of 41 g of
5 polymer/mol of catalyst/h, said polymer possessing the following characteristics: $M_n = 12\,900$. The chain incorporation of the monomer is isotactic ($mm > 95\%$).

Example 7:

20 ml of distilled toluene are introduced,
10 using a syringe, into a Schlenk tube (dried at 100°C for 2 h beforehand), connected to an argon line and equipped with a septum for introducing the reactants and with a magnetic stirrer. The toluene is degassed and then saturated with argon. Precursor B (40 mg) is
15 introduced and the solution is stirred at ambient temperature until its dissolution is complete. The catalytic solution is degassed three times, then a pressure of 1 bar of hydrogen is introduced. Hydrogenation is carried out at ambient temperature for
20 30 minutes. The solution turns from colorless to a vivid yellow. The hydrogen is subsequently driven off by a stream of argon (5 min). Then 2 ml of 1-pentene are introduced through the septum using a syringe. Polymerization is continued at 20°C for 2 hours.
25 Thereafter, 2 ml of methyl methacrylate are introduced with the septum. The solution changes in appearance to become opaque. The copolymerization is then continued for 2 hours. To neutralize the catalyst at the end of the reaction, 10 ml of methanol are injected. The
30 precipitated polymer is then isolated by centrifuging and dried under vacuum for 3 hours. The polymer at this point has a sticky white appearance (presence of polyolefin characterized by a bimodal GPC possessing two maximum peaks of mass approximately 3 000 and
35 60 000). The mixture of polymers is subsequently washed with twice 10 ml of hexane (with stirring in hexane for 2 hours), which then allows the olefinic homopolymer to be removed with 10 ml of methanol. 0.21 g of polymer is

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collected, corresponding to an activity of 5.2 g of polymer/g of catalyst, said polymer possessing the following characteristics: proportion of 1-pentene = 20% by weight, proportion of MMA = 80% by weight, Mn = 45 400. The poly(1-pentene) block is isotactic (mm > 95%).

Example 8:

The procedure of example 7 is repeated, replacing precursor B by 40 mg of precursor C, and replacing the 1-pentene by 2 ml of 1-hexene and the MMA by 2 ml of caprolactone. The polymer possesses the following characteristics: proportion of 1-hexene = 12% by weight, proportion of caprolactone = 88% by weight, Mn = 32 000. The poly(1-hexene) block is isotactic (mm > 95%).

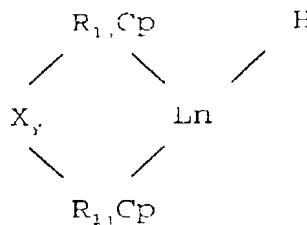
Example 9:

Precursor B (100 mg) is introduced into a Schlenk tube (dried at 100°C for 2 h beforehand) connected to an argon line and equipped with a septum for introducing the reactants and with a magnetic stirrer. 3 ml of 1-hexene are introduced through the septum using a syringe, and the mixture is degassed three times and held under vacuum. A pressure of 1 bar of hydrogen is then introduced. The polymerization starts immediately, characterized by an exotherm. The reaction mixture becomes highly viscous and the reaction is continued at 20°C for 3 minutes. Thereafter, 2 ml of caprolactone are introduced via the septum. The polymerization is then continued for 1 hour. To neutralize the catalyst at the end of the reaction, 10 ml of methanol are injected. The precipitated polymer is then isolated by centrifuging, washed with methanol and dried under vacuum for 3 hours. The polymer is in the form of a dry, nontacky powder. 0.45 g of polymer is collected, corresponding to an activity of 4.5 g of polymer/g of catalyst, said polymer possessing the following characteristics: proportion of 1-hexene = 4.5% by weight, proportion of

Amend

CLAIMS

1. A method of preparing block copolymers, comprising the steps of polymerizing a first monomer
 5 consisting of an alpha-olefin containing from 3 to 20 carbon atoms into a first, isotactic block, using a catalyst, then polymerizing at least one second monomer,
 said catalyst being in the form of a hydride complex of
 10 a trivalent metal from the rare earth group, having the formula I:



in which:

- Cp is a cyclopentadienyl radical;
 15 R_1 , identical or different at each occurrence, is a substituent of the cyclopentadienyl group and is an alkyl radical or a silicon-containing hydrocarbon radical, unsubstituted and containing from 1 to 6 carbon atoms;
 20 j , identical or different at each occurrence, is 1, 2 or 3;
 X is a divalent alkylene radical containing from 1 to 20 carbon atoms or $Si(R)_2$ in which R is an alkyl radical having from 1 to 4 carbon
 25 atoms;
 y is 1 or 2;
 Ln is Y or Sm.
2. The method as claimed in claim 1, wherein, in the formula I, R_1Cp is the group 2-Me₃Si, 4-Me₂tBuSiCp
 30 or the group 2-Me₃Si, 4-tBuCp.
3. The method as claimed in claim 1 or 2, wherein the catalyst is Me₂Si(2-Me₃Si, 4-Me₂tBuSiCp)₂YH or Me₂Si(2-Me₃Si, 4-tBuCp)₂SmH.

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4. The method as claimed in one of claims 1 to 3, wherein the catalyst is racemic.
5. The method as claimed in one of claims 1 to 4, wherein the catalyst is generated in situ in the presence of at least one portion of the first monomer.
6. The method as claimed in one of claims 1 to 5, wherein the catalyst is prepared by hydrogenation of the alkyl precursor.
7. The method as claimed in one of claims 1 to 6, wherein the blocks are homopolymers or random copolymers.
8. The method as claimed in one of claims 1 to 7, wherein the block copolymer comprises a block of the second monomer which is a vinyl, vinylidene or lactone compound.
9. The method as claimed in claim 8, wherein the vinyl or vinylidene compound is represented by the formula $H_2C=CR'Z$ in which R' is hydrogen or an alkyl radical having from 1 to 12 carbon atoms and Z is an electron-withdrawing radical.
10. The method as claimed in claim 9, wherein the vinyl or vinylidene compound is an ester of an unsaturated carboxylic acid.
11. The method as claimed in one of claims 8 to 10, wherein the poly-alpha-olefin is crystalline.
12. The method as claimed in one of claims 1 to 11, wherein the second monomer is polar.
13. The method as claimed in one of claims 1 to 12, for preparing a poly-alpha-olefin/PMMA or poly-alpha-olefin/polylactone copolymer.
14. The method as claimed in one of claims 1 to 10, wherein the block copolymer comprises a block of the second monomer which is an alpha-olefin.
15. The method as claimed in claim 14, wherein the first poly-alpha-olefin is crystalline and the second poly-alpha-olefin is crystalline.
16. The method as claimed in claim 15, for preparing a PP/PE copolymer.

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17. The method as claimed in claim 13, wherein the first poly-alpha-olefin is crystalline and the second poly-alpha-olefin is amorphous.
18. The method as claimed in claim 17, for
5 preparing a PP/EP copolymer.
19. The method as claimed in one of claims 1 to 18, wherein the block copolymer comprises a first iPP block.
20. A copolymer comprising a first block of a
10 crystalline polyolefin derived from an alpha-olefin containing from 3 to 20 carbon atoms and a second block of an amorphous polyolefin, with the exception of a PP/EP copolymer having a molecular mass M_n of less than or equal to 16 000 and a polydispersity index of
15 between 3 and 3.3.
21. The copolymer as claimed in claim 20, which is a PP/EP copolymer.
22. A copolymer comprising a first block of a crystalline polyolefin derived from an alpha-olefin
20 containing from 3 to 20 carbon atoms and a second block of a crystalline polyolefin.
23. The copolymer as claimed in one of claims 20 to 22, wherein the first block is isotactic.
24. A copolymer comprising a first block of an
25 amorphous polyolefin derived from an alpha-olefin containing from 3 to 20 carbon atoms and a second block of an amorphous polyolefin.
25. The copolymer as claimed in one of claims 20 to 24, wherein the blocks are homopolymers or random
30 copolymers.

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DEMANDE INTERNATIONALE PUBLIÉE EN VERTU DU TRAITÉ DE COOPÉRATION EN MATIÈRE DE BREVETS (PCT)

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(54) Title: METHOD FOR COPOLYMERIZATION AND RESULTING COPOLYMERS

(54) Titre: PROCEDE DE COPOLYMERISATION ET COPOLYMERES AINSI OBTENUS

(57) Abstract

The invention concerns a method for preparing block copolymers comprising steps which consist in: polymerising a first monomer using an organolanthanide catalyst wherein said catalyst in the form of a hydride complex of a trivalent metal from the group of rare earths; then in polymerising at least a second monomer. The invention also concerns block copolymers whereof the blocks are polyolefins.

(57) Abrégé

L'invention a pour objet un procédé de préparation de copolymères blocs comprenant les étapes de polymérisation d'un premier monomère à l'aide d'un catalyseur organolanthanide dans lequel ledit catalyseur est sous la forme d'un complexe hydrure d'un métal trivalent du groupe des terres rares, puis polymérisation d'au moins un second monomère. L'invention a encore pour objet des copolymères blocs dont les blocs sont des polyoléfines.

DECLARATION AND POWER OF ATTORNEY

As below named inventors, We hereby declare that:

My residence, post office address and citizenship are as stated below next to my name,

I believe I am the original, first and joint inventor of the subject matter which is claimed and for which a patent is sought on the invention entitled:

METHOD FOR COPOLYMERIZATION AND RESULTING COPOLYMERS

the specification of which was filed on September 21, 2001 and has:

☐ attached hereto

☒ an International Filing Date of March 14, 2000
and an International application number of 09/937,090
and amended on _____ (if applicable).

☒ was described and claimed in PCT Application No. PCT/FR00/00614
filed on March 14, 2000 and amended under Article 19 on _____

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose all information I know to be material to patentability in accordance with Title 37, Code of Federal Regulation, § 1.56.

I hereby claim foreign priority benefits under Title 35, United States Code § 119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

Prior Foreign Application(s)

<u>Serial Number</u>	<u>Country</u>	<u>Filing Date</u>	<u>Priority Claimed</u> (Y/N)
99 03 669	FR	3/24/99	Y
PCT/FR00/00614	PCT	3/14/00	Y

I hereby claim the benefit under Title 35, United States Code, § 120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code § 112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, § 1.56(a) which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

Serial Number

Filing Date

Status

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

And I hereby appoint:

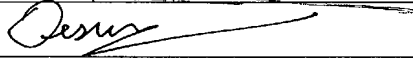
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C. Joseph Laughon, II	Reg. No. 31,389	David S. Figatner	Reg. No. 44,106
Leora Ben-Ami	Reg. No. 32,455	Steven J. Lever	Reg. No. 46,871
Robert D. Schaffer	Reg. No. 33,775		

all of the firm of Clifford Chance Rogers & Wells LLP, 200 Park Avenue, New York, New York 10166-0153, my attorney with full power of substitution and revocation, to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith.

Address all communications to:

Joseph Levi, Esq.
Clifford Chance Rogers & Wells LLP
200 Park Avenue, New York, NY 10016
(212) 878-8564

Wherefore I request that Letters Patent be granted to me for the invention or discovery described and claimed in the foregoing specification and claims, and I hereby subscribe my name to the foregoing specification and claims, declaration, power of attorney, and this petition.

Full name of inventor # 1		Guillaume Desurmont	
Inventor's signature		Date	05/07/2002
Residence	Elf Atochem Japan Kyoto Technical, Center SCB=3 Kyoto Research Park, 1 Awatacho, Chudoji, Shimogyo-Ku, Kyoto 600-8815, Japan JAX		
Citizenship	FRENCH		
Post Office Address	Elf Atochem Japan Kyoto Technical, Center SCB=3 Kyoto Research Park, 1 Awatacho, Chudoji, Shimogyo-Ku, Kyoto 600-8815, Japan		

NYA 379671.1

As below named inventors, We hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and joint inventor of the subject matter which is claimed and for which a patent is sought on the invention entitled:

the specification of which was filed on September 21, 2001 and has:

☐ attached hereto

☒ an International Filing Date of March 14, 2000
and an International application number of 09/937,090
and amended on _____ (if applicable).

☒ was described and claimed in PCT Application No. PCT/FR00/00614 filed on March 14, 2000 and amended under Article 19 on

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose all information I know to be material to patentability in accordance with Title 37, Code of Federal Regulation, § 1.56.

I hereby claim foreign priority benefits under Title 35, United States Code § 119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

Prior Foreign Application(s)

<u>Serial Number</u>	<u>Country</u>	<u>Filing Date</u>	<u>Priority Claimed (Y/N)</u>
99 03 669	FR	3/24/99	Y
PCT/FR00/00614	PCT	3/14/00	Y

I hereby claim the benefit under Title 35, United States Code, § 120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code § 112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, § 1.56(a) which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

Serial Number

Filing Date

Status

And I hereby appoint:

all of the firm of Clifford Chance Rogers & Wells LLP, 200 Park Avenue, New York, New York 10166-0153, my attorney with full power of substitution and revocation, to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith.

Joseph Levi, Esq.
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(212) 878-8564

Full name of inventor # 1		Guillaume Desurmont	
Inventor's signature			Date
Residence	Elf Atochem Japan Kyoto Technical, Center SCB=3 Kyoto Research Park, 1 Awatacho, Chudoji, Shimogyo-Ku, Kyoto 600-8815, Japan		
Citizenship			
Post Office Address	Elf Atochem Japan Kyoto Technical, Center SCB=3 Kyoto Research Park, 1 Awatacho, Chudoji, Shimogyo-Ku, Kyoto 600-8815, Japan		

Full name of inventor # 2		Hajime Yasuda	
Inventor's signature		<i>H. Yasuda</i>	Date <i>July 2, 2002</i>
Residence	531-401 Iida, Hachihonmatsucho, Higashihiroshima-shi, Hiroshima-Ken, Japan <i>JAX</i>		
Citizenship	<i>Japanese</i>		
Post Office Address		531-401 Iida, Hachihonmatsucho, Higashihiroshima-shi, Hiroshima-Ken, Japan	

Full name of inventor # 3		Jean Malinge	
Inventor's signature			Date
Residence	Maison Lasserre, 64300 Loubieng, France		
Citizenship			
Post Office Address		Maison Lasserre, 64300 Loubieng, France	

Docket No. 6680-010

DECLARATION AND POWER OF ATTORNEY

As below named inventors, We hereby declare that:

My residence, post office address and citizenship are as stated below next to my name,

I believe I am the original, first and joint inventor of the subject matter which is claimed and for which a patent is sought on the invention entitled:

METHOD FOR COPOLYMERIZATION AND RESULTING COPOLYMERS

the specification of which was filed on September 21, 2001 and has:

☐ attached hereto

☒ an International Filing Date of March 14, 2000
and an International application number of 09/937,090
and amended on _____ (if applicable).

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<u>Serial Number</u>	<u>Filing Date</u>	<u>Status</u>
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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

And I hereby appoint:

John E. Kidd	Reg. No. 19,916	Michael M. O'Shea	Reg. No. 35,631
Victor Siber	Reg. No. 25,149	Joel N. Bock	Reg. No. 36,456
Margaret B. Kelley	Reg. No. 29,181	Gerard P. Norton	Reg. No. 36,621
Philip E. Roux	Reg. No. 31,295	John T. Johnson	Reg. No. 37,363
Michael J. Pantuliano	Reg. No. 18,971	Frank C. Cimino	Reg. No. 39,945
Joseph P. Kincart	Reg. No. 43,716	Nada Jain	Reg. No. 41,431
James V. Mahon	Reg. No. 41,966	Mitchell S. Feller	Reg. No. 42,530
Joseph Levi	Reg. No. 41,152	David F. Ries	Reg. No. 43,046
Victor J. Geraci	Reg. No. 38,157	Anne M. Coughlin	Reg. No. 43,564
C. Joseph Laughon, II	Reg. No. 31,389	David S. Figatner	Reg. No. 44,106
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Citizenship			
Post Office Address	Elf Atochem Japan Kyoto Technical, Center SCB=3 Kyoto Research Park, 1 Awatacho, Chudoji, Shimogyo-Ku, Kyoto 600-8815, Japan		

Full name of inventor # 2		Hajime Yasuda	
Inventor's signature		Date	
Residence	531-401 Iida, Hachihonmatsucho, Higashihiroshima-shi, Hiroshima-Ken, Japan		
Citizenship			
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3rd

Full name of inventor # 3		Jean Malinge	
Inventor's signature	Jean Malinge	Date	2 juillet 2002
Residence	Maison Lasserre, 64300 Loubieng, France FRX		
Citizenship	French		
Post Office Address	Maison Lasserre, 64300 Loubieng, France		